

# STUDY ON HYDROGEN DONATION ABILITY OF RESIDUE HYDROCRACKING SYSTEM CATALYZED BY OIL-SOLUBLE AND WATER-SOLUBLE CATALYSTS

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Molybdenum-based oil-soluble and iron-based water-soluble catalyst precursors were separately used in catalytic hydrocracking systems of Liaohe vacuum residue in order to investigate the hydrogen donation ability of mild hydrocracking products. The catalytic hydrocracking tests were conducted in an 100ml autoclave, at 430°C, 30min, 7.0MPa initial hydrogen and 50°C, 500ppm catalysts (based on metal in feed). Anthracene (ANT) was used as a hydrogen acceptor to react, under conditions of 405°C, 2MPa N<sub>2</sub> and 30 minutes, with the atmospheric residue (AR) of hydrocracking products to determine the hydrogen donation ability of the AR. Thus, the hydroaromatic species in the AR might donate active hydrogen to anthracene, which make anthracene change to dihydroanthracene (DHA). GC technique was used to quantify the DHA formation, which was indirectly indicative of the hydrogenation activity of different hydrocracking catalysts. The results showed that Fe-based water-soluble catalysts have little ability to hydrogenate the polycyclic aromatics to hydroaromatics, the hydrogen donors, though they could inhibit coke formation when used in relatively large amount. However, Mo-based oil-soluble catalyst has higher hydrogenation activity, and even could promote hydroaromatics generation. These secondary hydrogen donors could act as a reservoir of active hydrogen and a complement to the active hydrogen molecules activated directly by catalysts in the subsequent hydrocracking stage.

**Key words:** hydrogen donation, catalytic hydrocracking, vacuum residue

## INTRODUCTION

Dispersed metal catalysts used in slurry phase hydrocracking of residue are commonly prepared either by the addition of finely divided inorganic powders to the residue, or by the addition of water- or oil-soluble metal salts to the heavy oils [1-8]. For the same metal, its oil-soluble salts seems more active than its water-soluble salts and its inorganic powders, as its oil-soluble salts can be homogeneously mixed into the heavy oil and can form superfine active catalyst particles after sulfidation [1,5]. For different metals, Mo, Ni, Co, Fe are most commonly used [1-8], of which Mo seems the most active in residue hydrocracking and Fe may be the lowest in their salt prices.

All these catalysts can suppress coke formation during residue hydrocracking by hydrogenating unstable polynuclear aromatic free radicals that are generated thermally [1,3]. Some may be quite active even in very low concentrations (100-200ppm, based on metal to residue), such as oil-soluble Mo-based catalysts [1,5]; some others can counterbalance the total catalytic activity only as in a large amount (1000-5000ppm), such as Fe-based water-soluble or powdered catalysts [1,6,7]. Hence, it seems that there is a little difference in coke suppression mechanism between these two relatively extreme catalysts. The present study uses anthracene (ANT) as a chemical probe to characterize the hydrogen donation ability of residue hydrocracking systems catalyzed respectively by Mo-based oil-soluble and Fe-based water-soluble catalysts. The hydroaromatic species in residue can donate hydrogen to anthracene and make the anthracene mainly change to dihydroanthracene (DHA) [9-12]. The hydrogen donation ability is indicative of inter- or intra-molecular hydrogen transfer between the donors and coke precursors free radicals. The higher is the hydrogen donation, the higher the coke suppression ability.

## EXPERIMENTAL

### Sample

Liaohe vacuum residue(>500°C) was collected from Liaohe Petrochemical Plant in March 1996. Carlo Erba 1160 elemental analyzer was used for C, H, N analysis; atomic absorption method was used to determine Ni, V, Fe and Ca contents. Average molecular weight was measured by using VPO method (benzene as solvent, 45°C) with Knauer molecular weight analyzer. The general properties of Liaohe vacuum residue are listed in Table 1.

### Catalytic hydrocracking of Liaohe vacuum residue

The experiments were carried in a 100ml FDW-01 autoclave reactor with an up-and-down stirrer at 120 times of reciprocation per minute. Initial pressure was 7.0MPa H<sub>2</sub> for catalytic hydrocracking.

Catalyst used in the hydrocracking reaction was Molybdenum-based oil soluble and iron-based water-soluble catalyst (ca.50~1000 ppm based on metal concentration in feed). The former was compatible with the vacuum residue and gave rise to the homogeneous system with the vacuum residue, and the later was emulsified into the vacuum residue to form emulsion system. After sulfidation by elemental sulfur at 320°C for 30 minutes (S/Metal atomic ratio=3/1), these catalyst precursors were in situ reacted to real active catalysts. Then, the temperature was raised to 430°C and kept at the temperature just for 30 minutes for hydrocracking reaction. After that, the reactor was quenched (cooled) to room temperature, the reactor gas was vented, and toluene slurry was prepared from the reactor contents. Any solids adhering to the reactor walls or internals was carefully scraped off. The slurry was then centrifuged and the toluene insoluble (TI or coke) were separated and washed (extracted) with boiling toluene by using quantitative filter paper. The solids were dried and weighed. The toluene soluble was distilled into several fractions. The results were listed in table 2.

#### Measurement of hydrogen donation abilities of Liaohu vacuum residue hydrocracking products

Anthracene (ANT) was used as a hydrogen acceptor to react, in a 50 cm<sup>3</sup> stainless steel tubular reactor with a 30 cm<sup>3</sup> quartz inner tubular microreactor, with >350°C fraction of the hydrocracking products under 405°C and 2MPa N<sub>2</sub> atmosphere. The feed charge is a mixture of 1-gram oil sample and 2 gram anthracene. Thus, the secondary hydroaromatics in >350°C fraction of hydrocracking products can donate active hydrogen to anthracene, which make anthracene change to 9,10-dihydroanthracene (DHA)[9-12]. The reaction products were analyzed by gas chromatography using a Varian3400 chromatograph equipped with a 30m×2.65um HP-5 (crosslinked 5% Ph Me silicon) column and a FID detector and naphthalene and DHA as the internal standards. The contents of DHA generated in the thermal reaction system were listed in table 3. The quantity of molar hydrogen accepted from one gram of charged oil sample could be calculated by following equation:

$$MN=Y_{DHA} \times W_{mix} / (M_{DHA} \times W_{oil})$$

Here, MN is the moles of hydrogen accepted from 1 gram of oil sample, Y<sub>DHA</sub> the yield of DHA in the thermal reaction system, W<sub>mix</sub> the weight of charged mixture of oil and ANT, M<sub>DHA</sub> the molecular weight of DHN and W<sub>oil</sub> the weight of charged oil sample. The MN values for different oil samples were also tabulated in table3.

## RESULTS AND DISCUSSION

### Distribution of hydrocracking products

It seems that the coke formation has a tendency to increase with the Mo-based catalysts at the early stage of Liaohu vacuum residue hydrocracking as indicated in table 2. This coke may largely consist of condensed-asphaltene. Under the induction of polar catalyst particles, the structure of asphaltene micellae may become loose, and asphaltene may be adsorbed by MoS<sub>2</sub> particles (with relatively higher polarity) and may condense on the particles, leading to the formation of toluene insoluble materials, a physically condensed state of asphaltene of higher polarity, not a real chemical coke. The more the MoS<sub>2</sub> catalysts, the stronger the induction to polar asphaltene may be, the more the initial coke will form, but the less the ratio of the coke to MoS<sub>2</sub>; and, relatively, the total catalyst activity is still high. The product distribution indicates that with increasing Mo-based catalyst, conversion to VGO seems to increase and the conversion to lighter product decreases, showing an increase in hydrogenation ability.

### Hydrogen donation ability of Liaohu vacuum residue and its hydrocracking products

This work aimed at determining the hydrogen donation abilities of Liaohu vacuum residue and its hydrocracking products, VGO(350 - 480°C) and hydrocracked vacuum residues (HVR), processed under different conditions. As table 3 indicated, the Liaohu Atmospheric residue has higher hydrogen-donating ability than its vacuum residue. The hydrogen-donating abilities of thermal cracked products of Liaohu vacuum residue are less than those of its catalytic hydrocracking products, showing that the catalysts could, at least, suppress the cracking of hydrogen-donating species in the residue reaction system. In comparison, Mo-based oil-soluble catalyst could give rise to higher hydrogen-donating abilities of its catalyzed hydrocracking products than Fe-based water-soluble catalyst. It seems that the hydrogen activated by Fe-based catalyst was not enough high to hydrogenate polycyclic aromatics to hydroaromatics, leading to only a little difference in hydrogen-donating abilities between its catalyzed products and thermal cracking products. The Mo-based catalysts might catalyze hydrogenation of some active polycyclic aromatics to hydroaromatics beside its high coke suppression ability by directly catalyzing hydrogenation of

polycyclic aromatic free radicals. The hydroaromatics generated in situ could act as hydrogen donors in subsequent reactions. The active hydrogen transfer from the hydrogen donors to polycyclic aromatic free radicals may be easier than the active hydrogen directly activated by the catalysts because the hydroaromatics are more compatible with the free aromatic radicals than the catalysts.

With the increase of Mo-based catalyst, the hydrogen-donating abilities of its catalyzed hydrocracking products increase. As Mo was over 160ppm, the hydrocracked vacuum residues were very near to Liaohe vacuum residue in hydrogen-donating ability. On the basis of one gram of Liaohe vacuum residue, the total hydrogen donations of its catalytically hydrocracked AR were  $4.56 \times 10^{-4}$ ,  $5.02 \times 10^{-4}$ ,  $6.25 \times 10^{-4}$ ,  $6.42 \times 10^{-4}$ ,  $7.01 \times 10^{-4}$ ,  $7.12 \times 10^{-4}$ , and  $7.14 \times 10^{-4}$  moles for no catalyst, 470ppm Fe, 74ppm, 86ppm, 168ppm, 316ppm and 619ppm Mo respectively. In comparison to 470ppm Fe, 86ppm Mo could make the AR a net gain of  $1.40 \times 10^{-4}$  moles of hydrogen donation. Except for direct free radical hydrogenation ability of Mo catalyst, the net gain of hydrogen donation ability might play a great role in coke suppression during further hydrocracking process. For example, prolonging hydrocracking time from 30minutes to 1hour could make the coke formation to increase from 1.6% to 5.7% as 470ppm Fe catalyst was used, and make the coke formation to increase from 0.2% to only 1.3% when 86ppm Mo-based catalyst was used.

## CONCLUSION

Anthracene was used as a chemical probe to determine the hydrogen donation ability of Liaohe vacuum residue and its mild catalytic hydrocracking products. In comparison to pure thermal cracking, the catalysis of Fe-based water-soluble catalysts was little in promoting the formation or in suppressing the cracking of the hydroaromatics--the secondary hydrogen donors, though Fe catalysts could inhibit coke formation when used in relatively large amount [1]. However, Mo-based oil-soluble catalyst has higher hydrogenation activity, and even could promote hydroaromatics generation in comparison to Fe-based catalyst. These secondary hydrogen donors could act as a reservoir of active hydrogen and a complement to the active hydrogen molecules activated directly by catalysts in the subsequent hydrocracking stage.

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Table 1 General properties of Liaohe vacuum residue (VR)

Density(20°), g./cm <sup>3</sup>	0.9976	SARA fractions:	
Viscosity(100°)/mm <sup>2</sup> .s <sup>-1</sup>	3375	Saturates, %	17.4
Pour point, °C	42	Aromatics, %	30.3
Flash point, °C	312	Resins, %	50.2
Carbon residue, %	19.0	nC7-Asphaltene, %	2.1
Elemental composition		Total Metal/PPM	258.6
C, %	87.0	Ni, ppm	122.6
H, %	11.4	V, ppm	2.9
S, %	0.43	Fe, ppm	37.5
N, %	1.08	Ca, ppm	95.6
H/C(Atomic ratio)	1.50	Ash, %	0.06

Table 2 Effect of catalysts on Liaohe vacuum residue hydroconversion  
(430°C, 7MPa initial hydrogen pressure, reaction time 30 min.)

Catalyst, ppm	<350°C, %	350-480°C, % (VGO)	>480°C, % (HVR)	Coke, %
none	23.0	22.5	52.7	1.8
Fe, 470	21.5	20.1	56.8	1.6
Mo, 74	14.0	18.0	68.0	0.2
Mo, 86	14.3	17.0	68.5	0.2
Mo, 168	13.4	17.3	69.1	0.2
Mo, 316	13.1	18.4	68.2	0.3
Mo, 619	12.9	20.0	66.6	0.5

Table 3. Hydrogen transfer in thermal reaction system  
of initial hydrocracking products of Liaohe residue

Oil Sample/ANT (m/m)	DHA generated in thermal reaction system	MN × 10 <sup>4</sup>
LHVR, (0.2170:1)	1.32%	8.22
LHAR, (0.1970:1)	1.26%	8.49
VGO(H <sub>2</sub> ), (0.5042:1)	1.99%	6.60
VGO(H <sub>2</sub> ,Fe470), (0.4879:1)	2.13%	7.22
VGO(H <sub>2</sub> ,Mo74), (0.5032:1)	2.39%	7.93
VGO(H <sub>2</sub> ,Mo86), (0.5058:1)	2.42%	8.00
VGO (H <sub>2</sub> ,Mo168), (0.5143:1)	2.59%	8.47
VGO (H <sub>2</sub> ,Mo316), (0.5042:1)	2.75%	9.12
VGO (H <sub>2</sub> ,Mo619), (0.4938:1)	2.72%	9.14
HVR (H <sub>2</sub> ), (0.5073:1)	1.79%	5.91
HVR (H <sub>2</sub> ,Fe470), (0.5083:1)	1.91%	6.30
HVR (H <sub>2</sub> ,Mo74), (0.5120:1)	2.16%	7.09
HVR (H <sub>2</sub> ,Mo86), (0.4742:1)	2.14%	7.39
HVR (H <sub>2</sub> ,Mo168), (0.5001:1)	2.41%	8.03
HVR (H <sub>2</sub> ,Mo316), (0.4934:1)	2.37%	7.97
HVR (H <sub>2</sub> ,Mo619), (0.4945:1)	2.42%	8.12

VGO--350-450°C fraction; HVR--hydrocracked vacuum residue.

LHVR--Liaohe vacuum residue; LHAR--Liaohe atmospheric residue.